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EFFECTS OF CHAIN ORIENTATION ON RAMAN AND BRILLOUIN SCATTERING --ETC(U)

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report #5 ✓	2. GOVT ACCESSION NO. AD-A101690	3. RECIPIENT'S CATALOG NUMBER Technical Report
4. TITLE (and Subtitle) Effects of Chain Orientation on Raman and Brillouin Scattering Spectra of Hydrostatically Extruded Polypropylene		5. TYPE OF REPORT & PERIOD COVERED 1411
7. AUTHOR(s) C. H. Wang and David B. Cavanaugh		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry University of Utah Salt Lake City, Utah 84112		8. CONTRACT OR GRANT NUMBER(s) N00014 79C 0507 Serial RC-607
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research 800 N. Quincy St., Arlington Va. 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE June 26, 1981
		13. NUMBER OF PAGES 19
		15. SECURITY CLASS. (of this report) unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release, distribution unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) A		
18. SUPPLEMENTARY NOTES Prepared for publication in the Journal of Applied Physics		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Raman and Brillouin scattering spectra Extruded polypropylene rods New theory on chain orientation and elastic constants		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Raman and Brillouin scattering techniques have been used to study the effect of chain orientation in uniaxially extruded isotactic polypropylene. The orientation parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ are obtained by measuring several Raman scattering intensities associated with the CH_2 rocking mode at 841 cm^{-1} . Both $\langle P_2 \rangle$ and $\langle P_4 \rangle$ parameters represent the average of the local orientational distribution of the polypropylene backbone. The Raman scattering result for $\langle P_2 \rangle$ is found in good agreement with the previous study using		

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Contract N00014 & (C 0507
Searial RC-607

Technical Report No. 5

Effects of Chain Orientation on Raman
and Brillouin Scattering Spectra of
Hydrostatically Extruded Polypropylene

by

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Prepared for Publication
in the
Journal of Applied Physics

June 26, 1981

Accession For
PTIS GR. 11
PTIS 1A
PTIS 1B
PTIS 1C
PTIS 1D
PTIS 1E
PTIS 1F
PTIS 1G
PTIS 1H
PTIS 1I
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EFFECTS OF CHAIN ORIENTATION ON RAMAN AND BRILLOUIN SCATTERING

SPECTRA OF HYDROSTATICALLY EXTRUDED POLYPROPYLENE

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ABSTRACT

Raman and Brillouin scattering techniques have been used to study the effect of chain orientation in uniaxially extruded isotactic polypropylene. The orientation parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ are obtained by measuring several Raman scattering intensities associated with the CH_2 rocking mode at 841 cm^{-1} . Both $\langle P_2 \rangle$ and $\langle P_4 \rangle$ parameters represent the average of the local orientational distribution of the polypropylene backbone. The Raman scattering result for $\langle P_2 \rangle$ is found in good agreement with the previous study using another vibrational band. The high frequency elastic constants C_{11} , C_{33} , C_{44} and C_{13} of extruded isotactic polypropylene are determined by Brillouin scattering. The elastic constants of deformed polymers have been related to the orientation parameters determined by Brillouin scattering. The result obtained for $\langle P_2 \rangle$ at high extension using Brillouin scattering is found to be smaller than that of Raman. The result suggests that the pair orientation correlation between segments is important in affecting the hypersonic velocity.

INTRODUCTION

It is now established that imposition of hydrostatic pressure or uniaxial stretch can cause substantial changes in the mechanical properties of solid polymers. These externally applied perturbations induce plastic deformation as well as molecular orientation. To date, x-ray diffraction, low frequency sonic modulus and birefringence techniques have been used to determine the degree of chain orientation in deformed solid polymers.

The study of laser Raman spectra and Raman intensity ratios of various vibrational modes at several scattering geometries is another method for obtaining molecular structural information in polymer solids. In Raman scattering, one deals with a second rank polarizability tensor and the measurement of vibrational Raman depolarization ratios can provide quantitative information about orientational order parameters $\langle P_2(\cos^2\theta) \rangle$ and $\langle P_4(\cos^2\theta) \rangle$.

Brillouin light scattering is a new technique which we have recently developed as a tool for the investigation of the effect of external mechanical deformation on the structure of polymers. The basic principle for Brillouin scattering is based upon the coupling of the dielectric tensor to the mechanical strain tensor according to the expression (given in the principal axis system)

$$\delta \epsilon_{ij} = n_i^2 n_j^2 \sum_{k,l} P_{ijkl} S_{kl} \quad (1)$$

where P_{ijkl} are Pockel's photoelastic constants, $\delta \epsilon_{ij}$ and S_{kl} are the

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change of the dielectric tensor and the strain tensor, respectively. Since the strain tensor of a polymer solid is affected significantly by mechanical perturbation, one expects that Brillouin scattering spectra can be used to characterize both the equilibrium and dynamic state of polymer solids.

However, previous Brillouin scattering studies of polymers deal with liquid or clear amorphous solid samples due to the experimental difficulty associated with a very strong central elastic peak which covers up the much weaker Brillouin sidebands. However, recent development of high-contrast interferometry has alleviated the experimental difficulty and allows opaque samples to be studied.

In this paper we report the result for extruded polypropylene rods which serve to demonstrate the application of Raman and Brillouin scattering techniques for the study of deformed polymers.

EXPERIMENTAL

Polypropylene rods were extruded at a temperature of 110°C . The high pressure container in the present version consists of an extrusion cylinder which has a 25 mm inner diameter. The die employed in this study has a throat of 60 mm diameter. An unextruded sample and samples with the extrusion ratio R_E equal to 3.0, 3.3, 4.8 and 6.3 were used for Raman scattering experiments.

Raman scattering were obtained using a Spex 1401 double grating monochromator coupled to the photon counting system. An argon ion laser
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tuned to 4880 Å was used for excitation. The slit width of the spectrometer

was adjusted to yield a spectral resolution of 2 cm^{-1} . The Brillouin scattering spectra were obtained using a Fabry-Perot interferometer operated in five passes. An argon ion laser equipped with an intracavity etalon tuned to a single frequency at about 4880 \AA was used for exciting the Brillouin spectrum. The free spectral ranges used are 33 and 40 GHz and the overall instrumental finesse is over 60. The incident laser polarization is selected with or without the use of a half-wave plate which rotates the laser polarization by 90° . The polarization of the scattered light is analyzed with a Gran-Thomson prism polarizer. Both 90° and back scattering ($\approx 180^\circ$) geometries are used to obtain the Brillouin spectra.

RESULTS AND DISCUSSION

The intensity ratios of various internal vibrational modes in the hydrostatically extruded isotactic polypropylene were measured. The 841 cm^{-1} band, which has been assigned as a CH_2 rocking mode with A_1 symmetry has been used to determine the orientation parameter of the polypropylene chain backbone. The method deals first with measurements of Raman intensity ratios R_1 and R_2 for 841 cm^{-1} band of polypropylene as a function of extrusion ratio. The intensity ratios R_1 and R_2 are defined as:

$$R_1 = I_{zy} / I_{zz} \quad (1-a)$$

$$R_2 = I_{zy} / I_{yy}$$

where the z axis is the axis of extrusion and the x and y axes are transverse to the extrusion axis. I_{ij} are the integrated Raman intensities with incident laser polarization along i and the polarization of the scattered light along j. Using the irreducible spherical tensor algebra, it can be shown that for a totally symmetric band with a Raman tensor given by (in terms of the point group of the vibration unit),

$$\underline{\underline{\alpha}} \quad (a) \quad = \quad \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix} \quad (2)$$

The various integrated intensities are given by ²

$$I_{xy} = A \beta^2 \left\{ \frac{1}{15} - \frac{1}{21} \langle P_2 \rangle + \frac{1}{35} \langle P_4 \rangle \right\} \quad (3-a)$$

$$I_{zy} = A \beta^2 \left(\frac{1}{15} + \frac{1}{25} \langle P_2 \rangle - \frac{4}{35} \langle P_4 \rangle \right) \quad (3-b)$$

$$I_{yy} = A \left\{ (\alpha^2 + \frac{4}{45} \beta^2 - \frac{2}{3} \alpha \beta + \frac{4}{63} \beta^2) \langle P_2 \rangle + \frac{3}{35} \beta^2 \langle P_4 \rangle \right\} \quad (3-c)$$

$$I_{zz} = A \left\{ (\alpha^2 + \frac{4}{45} \beta^2 + \frac{4}{3} \alpha \beta + \frac{8}{63} \beta^2) \langle P_2 \rangle + \frac{8}{35} \beta^2 \langle P_4 \rangle \right\} \quad (3-d)$$

where A is a constant determined by the geometry factor, the incident wavelength of light, etc. α and β are respectively, the average value of the Raman tensor given by $\alpha = \frac{1}{3} (2a + b)$ and anisotropy given by $\beta = (b-a)$. The quantities $\langle P_2 \rangle$ and $\langle P_4 \rangle$ are the orientation parameters given by

$$\langle P_i \rangle = \int P_i f(\Omega) d\Omega \quad (4)$$

where $f(\Omega)$ is the orientation distribution function of the partially oriented polymer chains. P_i is the Legendre polynomial of order i . $\langle P_2 \rangle$ is Hermann's orientation parameter and $\langle P_4 \rangle$ is uniquely determined in Raman spectroscopy.

From Eqs. (1) and (3), one can relate the experimentally measured intensity ratios to the orientation parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$, provided that the α/β ratio is independently determined. In the isotropic phase the orientation parameters vanish, and one obtains the well known expression

$$R_{\text{iso}} = \frac{3\beta^2}{4\beta^2 + 45\alpha^2} = R_1 = R_2 \quad (5)$$

This quantity have been measured for the 841 cm^{-1} band in molten polypropylene, from which we have determined the α/β ratio to be equal to 0.403 ± 0.016 . Since the α/β is generally insensitive to the temperature variation, we assume this value to be applicable for the oriented polypropylene.

Knowing the α/β value and with the help of Eqs. (3), we have calculated $\langle P_2 \rangle$ and $\langle P_4 \rangle$ from the measured values of R_1 and R_2 . The determined $\langle P_2 \rangle$ and $\langle P_4 \rangle$ values are very close to the ones determined previously using a CH_2 twisting mode at 1256 cm^{-1} . Both $\langle P_2 \rangle$ and $\langle P_4 \rangle$ are found to ⁽²⁾ increase with increasing the extrusion ratio.

Consider now the Brillouin light scattering technique. In Brillouin scattering, light is inelastically scattered from thermal phonons to produce side bands which are shifted from the incident frequency by an amount ν (in Hz) given by:

$$\nu = \frac{V}{\lambda_0} (n_1^2 + n_s^2 - 2n_1 n_s \cos)^{1/2} \quad (6)$$

where θ is the scattering angle, λ_0 is the wavelength of the incident light in vacuo, V is the acoustic phonon velocity; n_i and n_s are, respectively, indices of refraction of the incident and scattered light waves.

The stress tensor which appears in Eq. (1) is related to elastic constants through Newton's equation of motion,

$$\rho \frac{\partial^2 u_i}{\partial t^2} = \sum_j \frac{\partial}{\partial x_j} T_{ij} = \sum_{jkl} C_{ijkl} \frac{\partial}{\partial x_j} S_{kl} \quad (7)$$

where T_{ij} is the stress tensor and C_{ijkl} is the elastic constant tensor. The damping effect is neglected in Eq. (7). Linear elasticity is also assumed in Eq. (7).

The acoustic phonon velocity for an extruded sample is uniquely described by the elastic constant matrix corresponding to a uniaxially symmetric system:

$$C_{ijkl} \equiv C_{mn} = \begin{pmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{13} & 0 & 0 & 0 \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} \end{pmatrix} \quad (8)$$

where $C_{66} = (C_{11} - C_{12}) / 2$.

Using Eqs. (7) and (8), the velocities of acoustic phonons propagating in various directions can be calculated in terms of the elastic constants and the density of the sample. The scattering activity of the acoustic phonons is related to the dielectric tensor fluctuation by Eq. (1). Thus, from the position of Brillouin frequency shift, the various elastic constants can be determined. For example, the Brillouin peak associated with the spectrum in the back scattering geometry $z(xx)\bar{z}$ is equal to (c.f. Eq. (6)).

$$v_3 = \frac{n_3}{\lambda_0} \left(\frac{C_{33}}{\rho} \right)^{\frac{1}{2}} \quad (9)$$

where the 3-axis is identified with the extrusion axis (the z-axis). n_3 is the index of refraction along the z-axis. The elastic constants C_{11} and C_{44} are determined in the $x(zz)\bar{x}$ and $y(zy)z$ scattering configurations, respectively, given by:

$$v_1 = v_2 = \frac{n_1}{\lambda_0} \left(\frac{C_{11}}{\rho} \right)^{\frac{1}{2}} \quad (10)$$

$$v_4 = \frac{1}{\lambda_0} (n_1^2 + n_3^2)^{\frac{1}{2}} \left(\frac{C_{44}}{\rho} \right)^{\frac{1}{2}} \quad (11)$$

Knowing C_{11} , C_{33} and C_{44} , we can determine C_{13} from the peaks observed from the 90° scattering $x(yy)z$ spectrum according to the expression:

$$v_{\pm} = \frac{1}{\lambda_0} \left[\frac{(n_1^2 + n_3^2)}{\rho} \right]^{\frac{1}{2}} \left\{ \frac{1}{2} (C_{11} + C_{33} + 2C_{44}) \pm \left[\frac{1}{4} (C_{11} - C_{33})^2 + (C_{13} + C_{44})^2 \right]^{\frac{1}{2}} \right\} \quad (12)$$

Shown in Fig. 1 are the representative Brillouin scattering spectra obtained in $x(zz)\bar{x}$ and $x(yy)z$ scattering configurations. As predicted, only one peak is observed in the $x(zz)\bar{x}$ spectrum and there are two peaks present in the $x(yy)z$ spectrum. The former spectrum corresponds to v_1 and the peaks in the latter spectrum correspond to v_+ and v_- .

From the peak positions and the density and index of refraction values which are obtained by independent measurements, we have obtained the elastic constants C_{11} , C_{33} , C_{44} and C_{13} for several extruded polypropylene rods. The elastic constants at several extrusion ratios are given in Table I. The elastic constant C_{66} (and hence C_{12}) is not shown due to the fact that for cylindrical symmetry the acoustic wave associated with the elastic constant C_{66} is not active in Brillouin scattering. One notes that at $R_e = 1$, C_{11} is equal to C_{33} . This result is consistent with the fact that unextruded samples have isotropic mechanical properties. One further notes that the elastic constant associated with the longitudinal wave (C_{11} and C_{33}) is higher than that associated with the transverse waves (C_{13} and C_{44}). This is easily understood from the fact that the interchain covalent bond is stronger than the intrachain van der Waals interaction, and the restoring forces for shear motion is much lower than that for compression. As the sample is extruded, C_{33} rises sharply and C_{11} decreases gradually. The sharp rise of C_{33} and the accompanying gradual decrease of C_{11} reflects the increasing alignment of chain segments along the extrusion axis as the sample is gradually deformed. The elastic constants C_{13} increases slightly, but C_{44} does not undergo significant change as the sample is extruded, thus suggesting that shear modulus due to the stress applied in the z -direction is insensitive to the orientation of chain segments.

The behavior of the elastic constants in extruded IPP is closely associated with the increased chain segment orientation. Using a simple model, Moseley has related the sonic velocity of the oriented polymers to the orientation parameter $\langle P_2 \rangle$ by:

$$\langle P_2 \rangle \equiv \frac{1}{2} \langle 3\cos^2\theta - 1 \rangle = 1 - \left(\frac{V_u}{V_3} \right)^2 = 1 - \left(\frac{C_{33}^0}{C_{33}} \right) \left(\frac{\rho}{\rho^0} \right) \quad (13)$$

where V_u is the longitudinal velocity of an unoriented sample and V_3 is the corresponding sonic velocity propagating along the extrusion axis. C_{33}^0 and ρ^0 are respectively the elastic constant and density of the unextruded sample. Using Eq. (13), we have calculated $\langle P_2 \rangle$ as a function of extrusion ratio. The calculated result is shown in Fig. 2, together with the Raman scattering results. The $\langle P_2 \rangle$ value obtained from Brillouin using Moseley's model is smaller than that from Raman scattering. Since Raman scattering result is quantitatively correct, the disagreement between Brillouin and Raman scattering results indicates that Moseley's theory for the orientation parameter is inadequate.

Moseley's theory is expected to fail at high orientation because V_3 does not approach infinity for a real sample, in contrast to the assumption made. Furthermore, the effect of plastic deformation as reflected by the change of intermolecular interaction will also play a role in perturbing the elastic constants. Moreover, since the elastic constants are fourth rank tensor not only the orientation parameter $\langle P_2 \rangle$ but also $\langle P_4 \rangle$ will contribute to the change of the elastic constants. Neglecting the effect of plastic deformation for a moment, we now examine how the externally imposed chain orientation will affect the elastic constants.

For this we assume that when the polymer is subject to extrusion, polymer chains are oriented on the average along the extrusion axis. The stress tensor of the deformed sample is related to that of the unperturbed state (T_i^0) by

$$T_{ij} = \sum_{k,l} A_{ik} A_{jl} T_{kl}^0 \quad (14)$$

When A_{ij} coefficients are elements of the rotation matrix which relates a chain segment in the initial orientation to its final orientation. The transformation is performed in two successive steps: first about the axis perpendicular to the axis of extrusion, followed by a rotation about extrusion axis (z). In terms of the Voigt notation, Equation (14) is written as:

$$T_\alpha = \sum_{\beta} M_{\alpha\beta} T_\beta^0 \quad (15)$$

with $\alpha, \beta = 1, 2, 3, 4, 5, 6$,

where the coefficients $M_{\alpha\beta}$ define a 6 X 6 transformation matrix and can be constructed from the A - matrix following the method developed by Bond. (8)

Using a similar transformation law for the strain tensor S and then carrying out the angular average about the azimuthal angle about the extrusion axis after substitution of Hooke's law; we obtain (assuming that the elastic constant tensor of a perfectly oriented sample has a cylindrical symmetry): (9)

$$\begin{aligned} C_{11} = & \frac{1}{21} (8 C_{11}^0 - 2 C_{13}^0 - 6 C_{33}^0 - 4 C_{44}^0) \langle P_2 \rangle \\ & + \frac{1}{35} (3 C_{11}^0 - 6 C_{13}^0 + 3 C_{33}^0 - 12 C_{44}^0) \langle P_4 \rangle \\ & + \frac{1}{15} (8 C_{11}^0 + 4 C_{13}^0 + 3 C_{33}^0 + 8 C_{44}^0) \end{aligned} \quad (16)$$

$$\begin{aligned}
C_{33} = & \frac{1}{21} (4 C_{13}^0 - 16 C_{11}^0 + 12 C_{33}^0 + 8 C_{44}^0) \langle P_2 \rangle \\
& + \frac{1}{35} (8 C_{11}^0 - 16 C_{13}^0 + 8 C_{33}^0 - 32 C_{44}^0) \langle P_4 \rangle \\
& + \frac{1}{15} (8 C_{11}^0 + 4 C_{13}^0 + 3 C_{33}^0 + 8 C_{44}^0)
\end{aligned} \tag{17}$$

$$\begin{aligned}
C_{13} = & \frac{1}{21} (C_{11}^0 + C_{33}^0 + 5 C_{13}^0 - 4 C_{44}^0 - 7 C_{12}^0) \langle P_2 \rangle \\
& + \frac{1}{35} (8 C_{13}^0 + 16 C_{44}^0 - 4 C_{11}^0 - 4 C_{33}^0) \langle P_4 \rangle \\
& + \frac{1}{15} (C_{11}^0 + C_{33}^0 + 8 C_{13}^0 - 4 C_{44}^0 + 5 C_{12}^0)
\end{aligned} \tag{18}$$

$$\begin{aligned}
C_{44} = & \frac{1}{21} \left(-\frac{5}{2} C_{11}^0 + C_{33}^0 - 2 C_{13}^0 + 3 C_{44}^0 + \frac{7}{2} C_{12}^0 \right) \langle P_2 \rangle \\
& + \frac{1}{35} (8 C_{13}^0 - 4 C_{11}^0 - 4 C_{33}^0 + 16 C_{44}^0) \langle P_4 \rangle \\
& + \frac{1}{15} (C_{11}^0 + C_{33}^0 - 2 C_{13}^0 + 6 C_{44}^0 + \frac{5}{2} C_{11}^0 - \frac{5}{2} C_{12}^0)
\end{aligned} \tag{19}$$

where C_{ij}^0 are the elastic constants of the completely oriented sample.

In the absence of intermolecular effects, Equations (16) - (19) will be rigorous. These equations relate the elastic constants of the perturbed sample to the orientation parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$. Furthermore, they provide a method of predicting the ultimate values of the elastic constants of a perfectly oriented sample. Equations (16) - (19) reduce to the correct limit for $\langle P_2 \rangle = \langle P_4 \rangle = 1$. Moreover, for unoriented samples.

$\langle P_2 \rangle = \langle P_4 \rangle = 0$, and for this case one has $C_{11} = C_{33}$ and $C_{44} = \frac{1}{2} \times (C_{11} - C_{13})$, as expected for the isotropic sample. Furthermore, it should be noted that Moseley's equation (Eq. (13)) cannot be obtained from Eq. (16).

Using Eqs. (16)-(19) together with the experimentally determined elastic constants and a computer least squares program, we have determined the orientation parameters and the intrinsic elastic constants relating to a completely oriented polypropylene rod. The values for C_{11}^0 , C_{33}^0 , C_{44}^0 and C_{13}^0 are found equal to 4.72, 15.1, 2.00 and 3.57×10^{10} dyne/cm², respectively. One notes that C_{33}^0 is a factor of 3.2 greater than C_{11}^0 . This is consistent with the fact that the velocity of sound is greater when transmitted parallel to the chain axis for a bundle of polymer chains than across the chain axis. However, since C_{33}^0 is only about three times larger than C_{11}^0 , Moseley's assumption for infinite C_{33}^0 for completely oriented chains is incorrect. Furthermore, in analyzing the Brillouin scattering data of polypropylene we have found that $\langle P_4 \rangle \neq \langle P_2 \rangle$. This result is in disagreement with that obtained using Raman scattering.² Careful examination of this result indicates that the closeness of $\langle P_4 \rangle$ to $\langle P_2 \rangle$ is a consequence of the fact that C_{44} remains unchanged when the extrusion ratio changes. Assuming the $\langle P_2 \rangle = \langle P_4 \rangle$ equality, it is possible to reduce Eqs. (16)-(18) to

$$C_{11} = (\lambda + 2\mu) (1 - \langle P_2 \rangle) + C_{11}^0 \langle P_2 \rangle \quad (20)$$

$$C_{33} = (\lambda + 2\mu) (1 - \langle P_2 \rangle) + C_{33}^0 \langle P_2 \rangle \quad (21)$$

and

$$C_{13} = \mu(1 - \langle P_2 \rangle) + C_{13}^0 \langle P_2 \rangle \quad (22)$$

where λ and μ are the two Lamé constants for an isotropic solid. For polypropylene, λ and μ are equal to 2.8 and 1.7×10^{10} dyne/cm², respectively. Since $(\lambda + 2\mu)$ is larger than C_{11}^0 , but less than C_{33}^0 , as the orientation of the polymer is increased, the elastic constant C_{11} is expected to decrease and C_{33} to increase, in agreement with the experimental result. In Fig. 2, one notes that at high extrusion ratio $\langle P_2 \rangle$ obtained using Brillouin scattering is less than that obtained with Raman scattering. The discrepancy is due to two factors. First, the plastic deformation which also occurs will give rise to a change in the intermolecular interaction, and results in enhancing the chain packing as well as fibril to fibril adhesion upon extrusion, thus also affecting the elastic constants. This effect is not included in the present calculation. However, this effect is probably not important in polypropylene, as the deformation of this polymer has been found to be well described by an affine transformation of the distances between cross-link points in the network.¹⁰ The second factor which is believed to be more important in polypropylene is associated with the fact that the sound velocity (or elastic constant) is a collective property and involves the single particle as well as the pair orientation effects. However, the orientation parameters as determined using Raman scattering is a local property. Thus, the orientation parameters determined

by Raman scattering need not be equal to that determined by Brillouin scattering unless the pair angular correlation effect turns out to be negligible. To relate the orientational parameters obtained from Raman to that from Brillouin scattering, a microscopic theory is needed. Work in this direction is currently in progress in our laboratory.

Acknowledgement:

We acknowledge the Office of Naval Research and the NSF Polymer Program, Grant No. DMR 79-12457 for providing financial support for this research. We also thank Dr. S. Staija for obtaining the Raman spectra of extruded polypropylene, and Dr. H. Kanetsuna for providing extruded polypropylene samples.

TABLE I

ELASTIC CONSTANTS (IN UNIT OF DYNE/CM² X 10¹⁰)

AS A FUNCTION OF EXTRUSION RATIO OF POLYPROPYLENE ROD

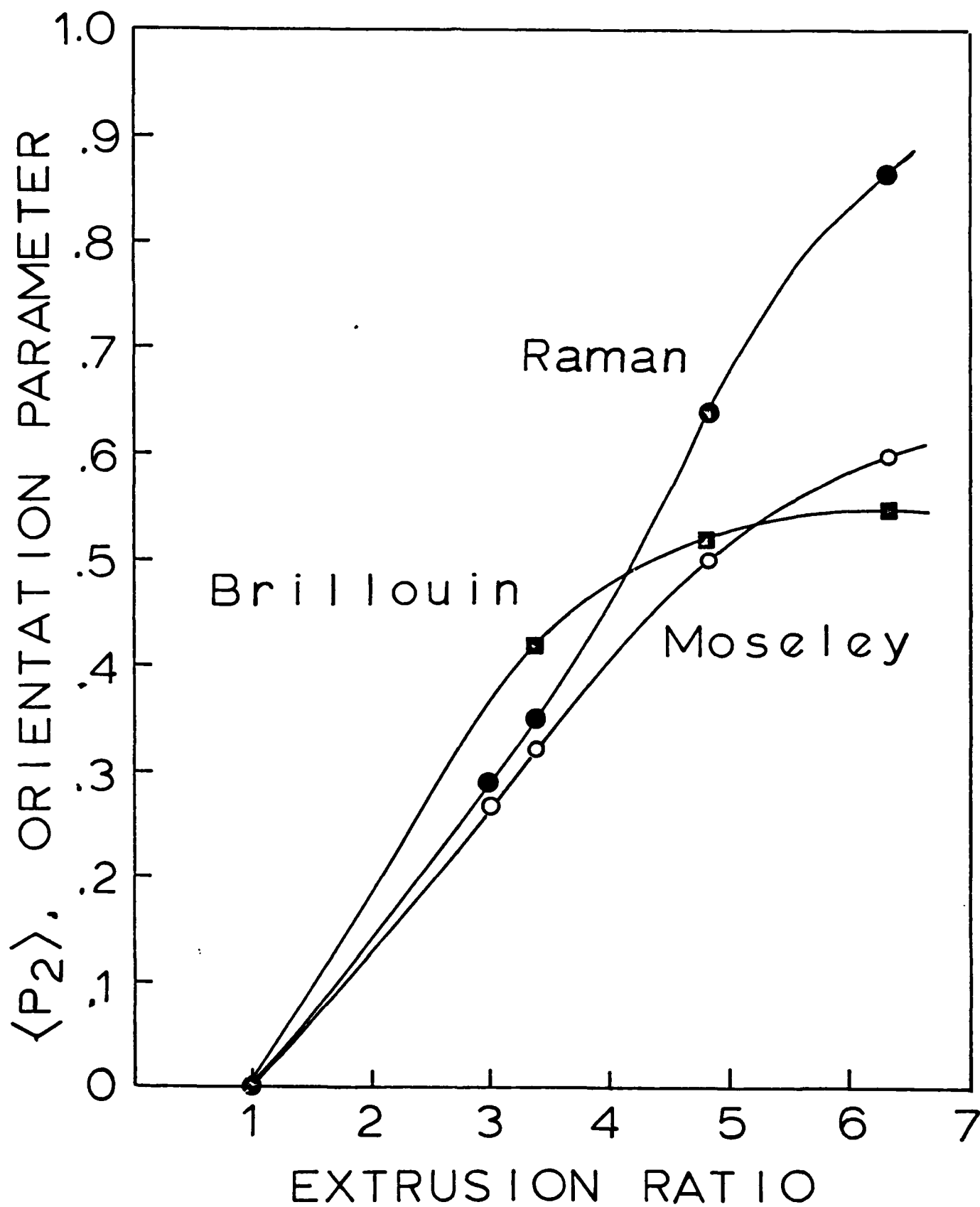
<u>EXTRUSION RATIO</u>	<u>C₁₁</u>	<u>C₃₃</u>	<u>C₄₄</u>	<u>C₁₃</u>
1.0	6.366	6.32	1.63	3.11
3.0	5.60	8.61	1.48	3.47
3.3	5.70	9.24	1.95	2.89
4.8	5.27	12.53	2.18	3.35
6.3	5.04	15.67	1.57	3.56

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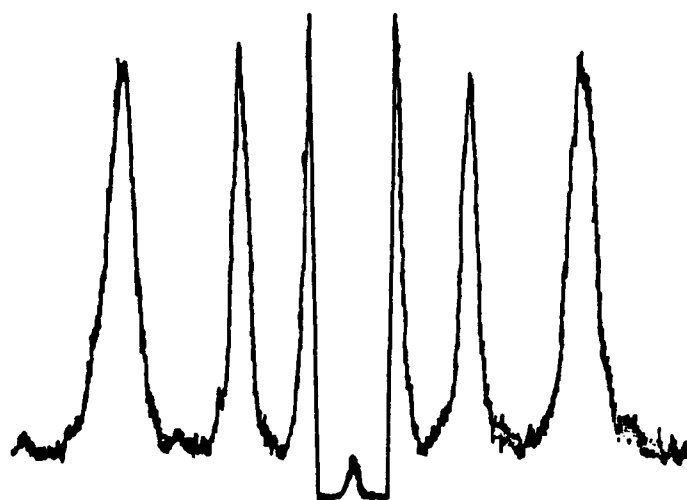
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FIGURE CAPTIONS

- Figure 1 Representative Brillouin scattering spectra obtained in $x(zz)x$ and $x(yy)z$ scattering configurations.
- Figure 2 Comparison of $\langle P_2 \rangle$ obtained using Raman, Brillouin and that using Mosel  y's model.

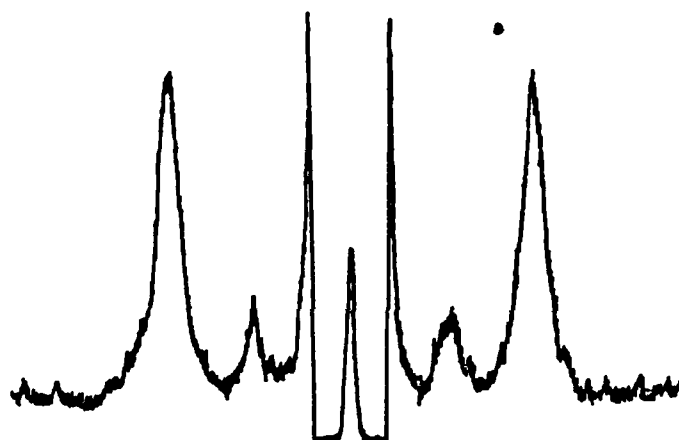


$R = 6.3$



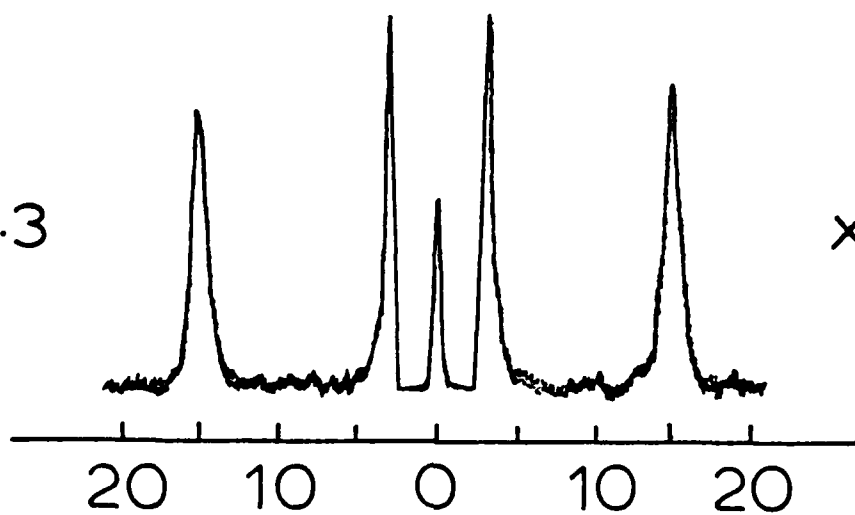
$z(YY)x$

$R_e = 3.3$



$z(YY)x$

$R_e = 6.3$



$x(ZZ)\bar{x}$

Brillouin Frequency (GHz)

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